



Applying quasi-isothermal thermogravimetry to determine degrees of oil conversion into biodiesel

Mário R. Cortes¹ · Joice F. de Queiroz¹ · Talina M. N. dos Santos¹ · Leandro F. Cavalheiro¹ · Marcelo Misutsu¹ · Luciana M. Ravaglia¹ · Glaucia B. Alcantara¹ · Luiz H. Vian¹ · Carlos E. D. Nazário¹ · Euclésio Simionatto² · Lincoln C. S. de Oliveira¹

Received: 5 May 2020 / Accepted: 8 April 2021 / Published online: 6 May 2021
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Abstract

Recent research has revealed the successful use of thermogravimetric analysis (TGA) in dynamic mode as an alternative method for determining degrees of oil conversion into biodiesel. This paper reports the results obtained with the use of TGA in quasi-isothermal mode (TGA-qISO) and with quantitative proton nuclear magnetic resonance (¹H qNMR) to investigate the compositions of blends of soybean oil and biodiesels (10:0, 8:2, 6:4, 4:6, 2:8, and 0:10, *m:m*). Also, reported are data acquired by applying a programmed sequence of TGA-qISO and gas chromatography with flame ionization detection (GC-FID) steps to a biodiesel witness sample and samples prepared by a partner laboratory. All the biodiesels were obtained by transesterification via the methyl route using homogeneous basic catalysis. Thermogravimetric curves (TG) clearly distinguished between mass losses caused by ester volatilization and those resulting from oil thermal decomposition. Ester contents calculated by TGA-qISO proved concordant with ¹H qNMR and GC-FID data, with maximum differences of around 0.5% and 1.4%, respectively.

Keywords Quasi-isothermal thermogravimetry · Ester content · Biodiesel

Introduction

Fossil fuels are the most crucial resources for the world's current energy supply [1]. Since burning these fuels generates greenhouse gases that contribute to climate change [2], alternative, renewable energy sources have attracted increasing interest, to minimize or even replace fossil fuels [3]. Biodiesels are low-toxicity, biodegradable biofuels devoid of sulfur or aromatic compounds. They produce less exhaust emissions, owing to high flash points, and can be obtained from a wide range of raw materials, including vegetable, seaweed, and microbial oils, animal fats, and even waste oils [4–6].

Biodiesel synthesis, however, generates contaminants such as intermediate glycerols, non-transesterified triglycerides, free fatty acids, and residual alcohols, which can pose serious operational problems, including deposit formation in engines, filter clogging, and fuel deterioration [7]. Quality requirements for biofuel commercialization include determining the degree of conversion of oil into biodiesel [8], using gas chromatography with flame ionization detection (GC-FID) [9]. This method, however, requires sample preparation with organic solvents such as *n*-heptane, toluene, and hexane—highly toxic and potentially polluting substances [9, 10].

Thermogravimetric analysis (TGA), although widely used to investigate biodiesel properties, including thermal stability, oxidation time, activation energy, and purity, has been employed to this end in dynamic heating mode, whereby mass loss is continuously recorded as the temperature is linearly increased [11–17]. This approach, however, may fail to distinguish between overlapping thermal decomposition and volatilization events, yielding significant ester measurement differences relative to the standard method [17, 19]. In quasi-isothermal thermogravimetric

✉ Lincoln C. S. de Oliveira
lincoln.oliveira@ufms.br

¹ Graduate Program in Chemistry, Institute of Chemistry, Universidade Federal de Mato Grosso Do Sul, Campo Grande, MS 79070-900, Brazil

² Graduate Program in Natural Resources, Universidade Estadual de Mato Grosso Do Sul, Dourados, Naviraí, MS 79950-000, Brazil

analysis (TGA-qISO), instead, a programmed sequence of furnace temperature modes (dynamic, isothermal, dynamic) is followed for data acquisition. Initial furnace temperature is linearly increased (dynamic mode) until mass loss does not exceed a pre-defined value, at which point the furnace operates in isothermal mode until mass stabilizes, subsequently resuming dynamic mode until a TG curve has been fully plotted [18]. The present investigation compared ester contents in blends of soybean oil and biodiesel as quantified by TGA-qISO and ^1H qNMR. In addition, values obtained using the programmed furnace operation sequence were compared against GC-FID data for samples prepared by a partner laboratory and a witness biodiesel sample.

Materials

Soybean oil (food grade) was purchased locally. Anhydrous methanol (Neon), potassium hydroxide (Neon), methyl heptadecanoate (used as an internal standard to quantify ester content by GC-FID; from Supelco), deuterated chloroform (CDCl_3 ; Aldrich), $\text{C}_{12}\text{H}_{10}$ (biphenyl, as an internal standard; Merck), and tetramethylsilane (TMS; CIL) were also employed.

Biodiesels will be abbreviated as follows (drawing on the first letter of the oilseed genus concerned):

<i>Glycine max</i> (soybean):	BdG
<i>Scheelea phalerata</i> ("bacuri"):	BdS
<i>Terminalia catappa</i> ("sete-copas"):	BdT

Experimental

Methyl biodiesel generation from uncombined soybean oil and soybean oil–biodiesel blends

The transesterification reaction was performed as per Verma and Sharma [19] on a 500 g oil mass at an oil-to-methanol molar ratio of 1:6. Reaction time was 1 h and the amount of catalyst 1% of the oil mass.

Blends of soybean oil and BdG were prepared at well-defined ratios (10:0, 8:2, 6:4, 4:6, 2:8, and 0:10, $m:m$) to better evidence correlations with mass losses on TGA-qISO curves. To this end, a mass corresponding to the established soybean oil content for each blend was weighed and a sufficient amount of biodiesel was added to complete a total mass of 10 g.

Biodiesel generation from *Scheelea phalerata* and *Terminalia catappa*

Biodiesels obtained from two oilseeds—*Scheelea phalerata* and *Terminalia catappa*—were kindly provided by partner researchers at the Chemical Technology Development Center of Universidade Estadual de Mato Grosso do Sul at Naviraí. These biodiesels had previously been investigated for thermal and oxidative stability in blends with soybean oil [20].

Ester quantification using GC-FID

Chromatography was performed according to the EN-1410 standard [21] in a GC 2010 gas chromatograph (Shimadzu) with an AOC-5000 sampler, equipped with a flame ionization detector. Stabilwax capillary columns (30 m; 0.25 mm; 0.25 μm) were used. Helium was the carrier gas, at a flow rate of 2.2 mL min^{-1} . Sample volume was 1 μL , injected at a split ratio of 1:50.

Both injector and detector temperatures were maintained at 250 $^{\circ}\text{C}$. Furnace temperature started at 60 $^{\circ}\text{C}$ (2 min isothermal regime), rising by 10 $^{\circ}\text{C min}^{-1}$ to 200 $^{\circ}\text{C}$ (followed by a 10 min isotherm), then by 5 $^{\circ}\text{C min}^{-1}$ to 240 $^{\circ}\text{C}$ (followed by a 7 min isotherm), comprising a total run time of 41 min. A methyl heptadecanoate solution at 10.02 mg mL^{-1} was prepared. A 50 mg mass from each sample was diluted in 1 mL of the internal standard solution.

Quantitative proton nuclear magnetic resonance spectroscopy (^1H qNMR)

Samples for ^1H qNMR analysis were prepared from 250 μL of blends of soybean oil and BdG, 250 μL of CDCl_3 , and 15 mg of $\text{C}_{12}\text{H}_{10}$ (internal standard). The resulting solution was transferred to a NMR tube (5 mm) and TMS vapor was added. The samples were prepared in triplicate.

^1H qNMR spectra were acquired at 20 $^{\circ}\text{C}$ on a 11.75 T Avance NEO 500 instrument (Bruker) equipped with a 5 mm multinuclear BBF Smart probe, observing ^1H at 500.13 MHz. Spectra were obtained applying a 30 $^{\circ}$ excitation pulse (zg30) with 16 scans, collecting 32 k points covering a spectral width of 23.8 ppm. Relaxation delay and acquisition time were 4 and 2 s, respectively, to guarantee a relaxation time longer than 7T1. NMR data were processed by applying an exponential multiplication by a factor of 0.3 Hz in free induced decay, and baseline and phase were manually corrected. All ^1H qNMR spectra were referred at 0.00 ppm to the TMS signal.

The integrals of signals were automatically calculated. The α -glycerol signal at 4.38–4.06 ppm (4H) for soybean oil, the methyl signal at 3.80–3.40 ppm (3H, OCH_3 group) for biodiesel, and the *o*-hydrogens from the internal standard

(biphenyl) at 7.67–7.48 ppm (4H) were used for quantification. Ester content was calculated using the following equation [22]. ^1H qNMR results were expressed in terms of biodiesel content (% *m:m*).

$$m_x = \frac{I_x N_{\text{std}} M_x m_{\text{std}} P_{\text{std}}}{I_{\text{std}} N_x M_{\text{std}} \times 100}$$

In this equation, m_x is the analyte mass (soybean oil or biodiesel); I_x and I_{std} are the integrated signal areas of analytes and internal standard, respectively; N_x and N_{std} are the number of protons in the signals from analytes and internal standard, respectively; M_x and M_{std} are the molar masses of analytes and internal standard, respectively; and P_{std} and m_{std} are the purity and weighed mass of the internal standard, respectively.

Quasi-isothermal thermogravimetric analysis

TGA-qISO curves for soybean oil blended with BdG, BdS, or BdT were acquired on a TGA-Q50 device (TA Instruments) under synthetic air and nitrogen atmospheres, at a flow rate of 60 mL min⁻¹ in the furnace and a heating ratio of 10 °C min⁻¹, using platinum crucibles as support and sample masses of 5.5 ± 2 mg.

Data acquisition proceeded as follows, both for blends and uncombined samples:

- stabilizing furnace temperature at 25 °C;
- conditional rule: interrupt next step if mass variation exceeds 2%;
- heating ramp at 10 °C min⁻¹ to 350 °C;
- conditional rule: interrupt next step if mass variation exceeds 2%;
- isothermal regime for 70 min or while mass change does not reach 2%;
- heating ramp at 10 °C min⁻¹ to 650 °C.

Results and discussion

Figure 1 depicts the TGA-qISO curves for blends of soybean oil and BdG acquired under oxidizing and inert atmospheres.

Three or four mass loss stages can be observed in the curves plotted under synthetic air. The first stage (100–200 °C) was attributed to biodiesel volatilization, while subsequent stages (250–600 °C) were attributed to triglyceride thermal decomposition [16, 23–25]. The two or three mass loss stages, visible in the curves acquired under a nitrogen atmosphere, were attributed to biodiesel volatilization (100–200 °C) and triglyceride thermal decomposition (350–400 °C) [26]. The curves reveal that the stages of oil thermal decomposition in the blends manifest at higher

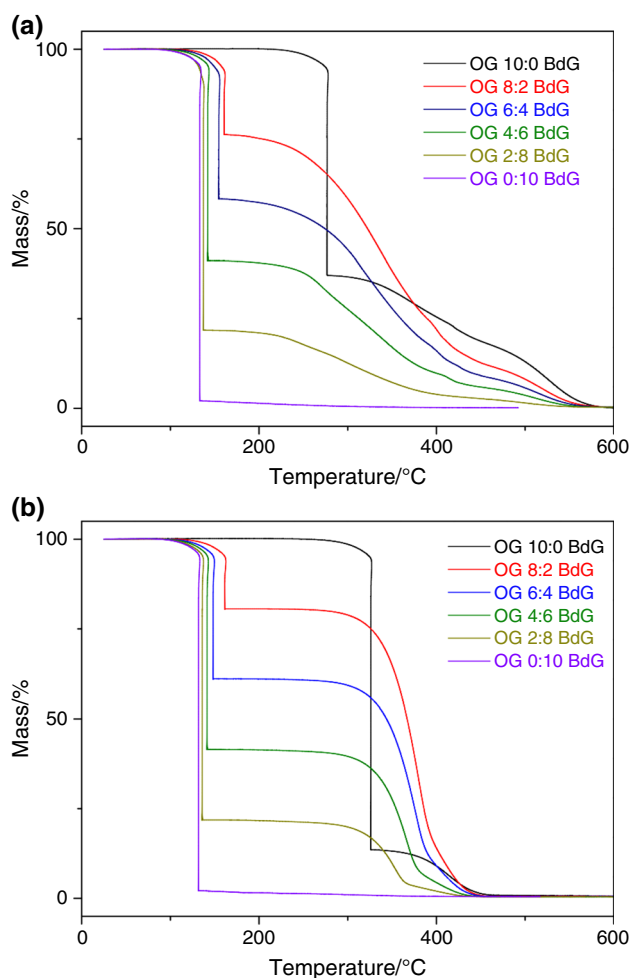


Fig. 1 Quasi-isothermal thermogravimetry curves acquired under synthetic air (a) and nitrogen (b) atmospheres for soybean oil (OG) and soybean oil biodiesel (BdG) blends

temperatures when nitrogen is the carrier gas, minimizing the likelihood of overlapping events such as partial triglyceride decomposition and biodiesel volatilization. However, even with shorter temperature intervals between stages, the results obtained for synthetic air also proved accurate.

Table 1 shows the mass losses taking place under synthetic air and nitrogen atmospheres in the 100–200 °C range and respective biodiesel contents, as quantified by ^1H qNMR. In this temperature range, no mass losses were detected for uncombined soybean oil under either atmosphere. Oil thermal decomposition started at 259 °C under synthetic air and 305 °C under nitrogen.

Figure 2 depicts analytical curves acquired under oxidizing and inert atmospheres, plotting mass losses (%) in the 100–200 °C range against biodiesel concentrations in the blends.

Table 2 shows linear regression data obtained under oxidizing and inert atmospheres.

Table 1 Mass losses (as per quasi-isothermal thermogravimetric analysis, TGA-qISO) relative to ester contents (calculated from quantitative proton nuclear magnetic resonance, ^1H qNMR) in the 100–200 °C range for blends of soybean oil (OG) and soybean oil biodiesel (BdG)

Blend	Mass/%; TGA-qISO under synthetic air	Mass/%; TGA-qISO under N_2	Ester content/%, $m:m$; ^1H qNMR
OG 10:0 BdG	–	–	0.8051 ± 0.36
OG 8:2 BdG	23.42 ± 1.35	19.51 ± 0.16	19.489 ± 0.02
OG 6:4 BdG	41.84 ± 0.87	39.00 ± 0.13	38.671 ± 0.06
OG 4:6 BdG	58.91 ± 0.01	58.66 ± 0.01	58.236 ± 0.45
OG 2:8 BdG	78.33 ± 0.10	78.17 ± 0.02	77.852 ± 0.43
OG 0:10 BdG	98.02 ± 0.02	98.19 ± 0.06	97.461 ± 0.15

Values expressed as means \pm SD ($n = 3$)

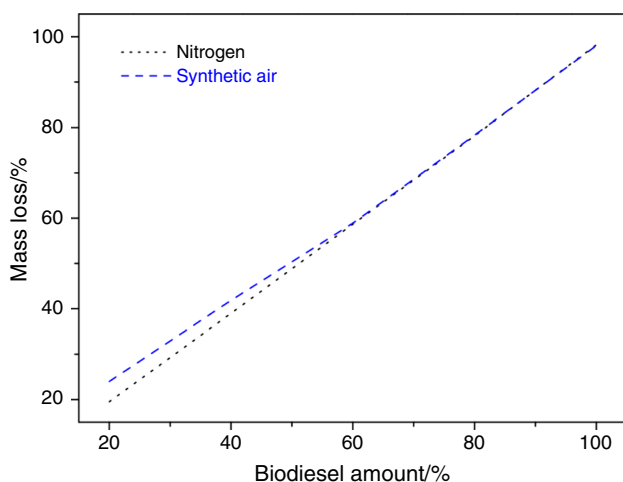


Fig. 2 Analytical curves for mass losses vs. biodiesel concentrations in biodiesel blends subjected to quasi-isothermal thermogravimetry under synthetic air and nitrogen atmospheres

Table 2 Linear regression data for mass losses vs. biodiesel concentrations in biodiesel blends subjected to quasi-isothermal thermogravimetry under synthetic air and nitrogen atmospheres

Atmosphere	Straight-line equation	R
Synthetic air	$y = 0.9228x + 4.8458$	0.9987
Nitrogen	$y = 0.9826x - 0.2545$	0.9999

Correlation coefficients exceeded 0.99 for both atmospheres, indicating a strong correlation between mass loss and biodiesel concentration in the blends [27].

To evaluate the efficiency of the programmed stepwise sequence, TGA-qISO curves were plotted for two biodiesel samples (BdS, BdT) prepared by a partner laboratory and for a BdG witness sample [16].

Table 3 Methyl ester compositions of biodiesels obtained from *Glycine max* (BdG) *Scheelea phalerata* (BdS), and *Terminalia catappa* (BdT), as determined by gas chromatography with flame ionization detection

Fatty acid	BdG/%	BdS/%	BdT/%
Caprylic acid (C8:0)	–	3.0	–
Capric acid (C10:0)	–	3.5	–
Lauric acid (C12:0)	–	29.0	–
Myristic acid (C14:0)	–	11.8	–
Palmitic acid (C16:0)	11.3	10.9	33.2
Stearic acid (C18:0)	3.5	3.6	4.6
Oleic acid (C18:1)	22.8	32.3	37.8
Linoleic acid (C18:2)	53.4	5.3	22.4
Linolenic acid (C18:3)	5.8	–	–
Total	96.8	99.7	98.0

Table 3 depicts the methyl ester compositions of BdG, BdS, and BdT, as quantified by GC-FID.

BdS methyl esters were predominantly saturated (61.8%, $m:m$, comprising 58.2% having 8 to 16-carbon chains). Unsaturated methyl esters accounted for 37.6% ($m:m$). For BdT, saturated and unsaturated contents were 37.8% and 60.2% ($m:m$), respectively, while for BdG these ratios were 14.8% and 82% ($m:m$), respectively (all esters with 16 to 18-carbon chains). Correlated with the TGA-qISO curves, these compositions revealed well-defined mass losses.

Figure 3 shows the TGA-qISO curves obtained for BdG, BdS, and BdT under oxidizing and inert atmospheres.

For BdT and BdG, however, a single mass loss step was detected under both atmospheres (133 and 134 °C for synthetic air; 133 and 131 °C for nitrogen, respectively)—a loss attributed to volatilization of saturated and unsaturated methyl esters (C16:0–C18:3). These results were corroborated by GC-FID (Table 3). Two volatilization steps were detected for BdS, irrespective of atmosphere. The first step (at roughly 96 °C), involved 56.75% mass loss, attributed to volatilization of shorter-chained (C8:0–C16:0) saturated methyl esters. The second step (at roughly 96–197 °C) involved 42.48% mass loss, attributed to longer-chained saturated (C18) and unsaturated (C16–C18) esters.

Table 4 compares the ester contents in BdS, BdT, and BdG quantified by GC-FID and by TGA-qISO under oxidizing and inert atmospheres.

Small differences, in the 0.50–1.43% range, were found between techniques (Table 4). These differences were significantly smaller than those reported elsewhere [16, 28]. However, published data show that roughly 1.2% of soybean oil biodiesel mass is constituted of 20-, 21-, and 22-carbon fatty acids [15], which were not detected in the present GC-FID analysis.

Figure 4 depicts mass loss curves (%) as a function of time (min) plotted for BdG samples (roughly 5.0 mg)

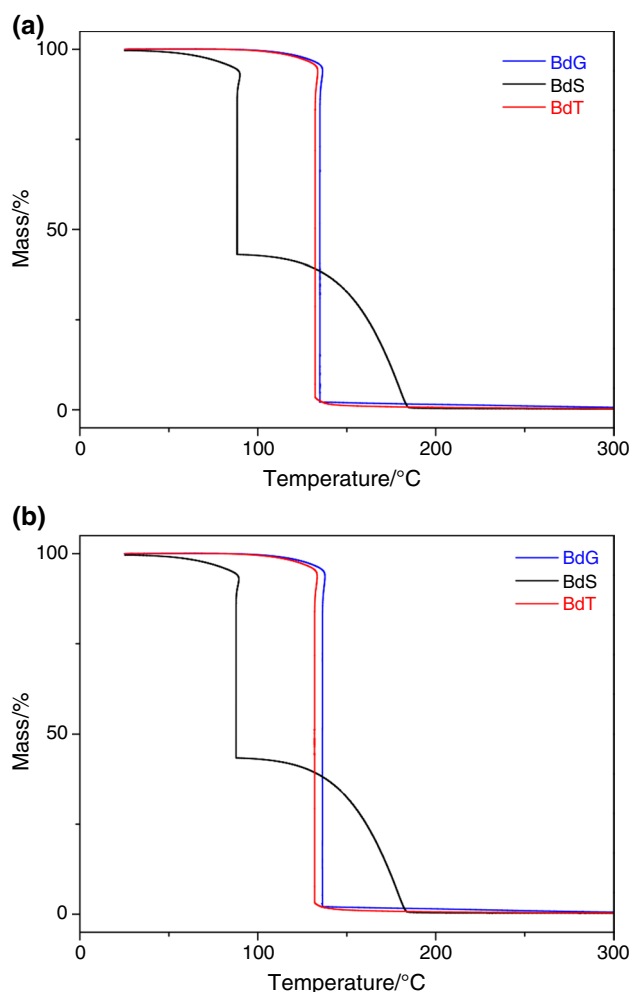


Fig. 3 Methyl biodiesel quasi-isothermal thermogravimetry curves acquired for biodiesels prepared from *Glycine max* (BdG), *Scheelea phalerata* (BdS), and *Terminalia catappa* (BdT) under synthetic air (a) and nitrogen (b) atmospheres

Table 4 Ester contents (%) in biodiesels obtained from *Glycine max* (BdG), *Scheelea phalerata* (BdS), and *Terminalia catappa* (BdT), as measured by gas chromatography with flame ionization detection (GC-FID) and by quasi-isothermal thermogravimetric analysis (TGA-qISO) under synthetic air and nitrogen atmospheres

Sample	GC-FID	TG(N ₂)	ΔGC– TG(N ₂)/%	TG(air)	ΔGC– TG(air)/%
BdG	96.8	98.16	1.40	98.18	1.43
BdS	99.7	98.88	0.82	99.22	0.50
BdT	98.0	98.93	0.95	98.85	0.86

subjected to TGA-qISO under a nitrogen atmosphere, revealing that 70 min of isothermal regime proved sufficient time for full thermal decomposition of biodiesel, allowing ester content to be accurately quantified.

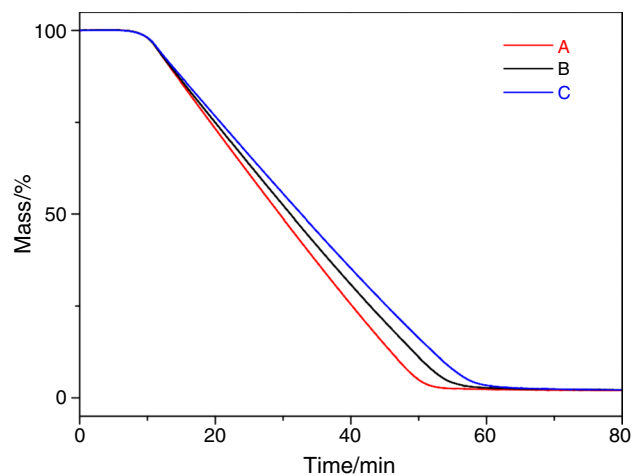


Fig. 4 Quasi-isothermal thermogravimetric curves for soybean oil methyl biodiesel samples as a function of time under a nitrogen atmosphere. **a** $m = 4.3830$ mg; **b** $m = 5.1660$ mg; **c** $m = 5.5490$ mg

Conclusions

The results obtained revealed TGA-qISO conducted with stepwise programming to be an accurate, reproducible method for quantifying ester content in biodiesels, with a maximum difference of 1.43% relative to the EN-14103 gas chromatography standard—a much smaller difference than that obtained with TGA conducted in dynamic heating mode [13, 16, 28]. Given its lower cost (requiring no pre-treatment of samples with toxic solvents), efficiency, and fast application, the proposed method has the potential to be employed as an alternative to official standards for biodiesel quality control.

Acknowledgements The authors are grateful for the financial support provided by the Mato Grosso do Sul Foundation for the Promotion of Teaching, Science, and Technology Development (Fundect-MS, Brazil) and the Brazilian Council for Scientific and Technological Development (CNPq). This investigation was partly funded by the Coordination for the Improvement of Higher Education Personnel (Capes, Brazil; finance code 001) and by the Universidade Federal de Mato Grosso do Sul.

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